MISCIBILITY OF LIQUIDS INFLUENCED BY RATE OF SHEAR

Extract from the Thesis
Submitted for the Degree of Doctor of Philosophy
to the Faculty of Science
of the University of Basle

by

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from

Johannesburg (South Africa)

St. Albans
Fisher, Knight & Co., Ltd.
1953

Accepted by the Faculty of Science on the recommendation of Professor W. Kuhn and Professor H. Kuhn,

Basle, the 1st of July, 1952.

W. KUHN
(Dean of the Faculty)

The Faculty of Science has by its decision of the 1st of July, 1952, authorized Mr. Alexander Silberberg to print this abbreviated form of his thesis which was accepted on the 1st of July, 1952. The complete paper, whose title is :

"Interfacial Tension and Phase Separation in
Two Polymer – Solvent Systems"

can be inspected at or borrowed from

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(*Reprinted from Nature, Vol. 170, p. 450, 1952*)

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WHETHER or not phase separation will occur in a liquid system is a question of the mutual solubilities of its components. It is usually assumed that, if pressure and relative composition are held constant, the temperature alone determines these solubilities and thereby decides the question of demixtion, that is, the general phase state of the system. From experiments which we have performed it appears, however, that the assumption of complete determination of solubility by temperature at constant pressure and relative composition requires considerable amendment. Our results show that in the case of certain demixed liquid–liquid systems the maintenance of a field of flow (stirring) can affect the solubility and thereby the miscibility of the phases as profoundly as a change of temperature of, say, 10° C., or a 1·15-fold dilution. It was found that even relatively mild flow conditions suffice to bring about complete reversal of phase separation in these systems.

The systems referred to are formed when two macromolecular solutes, for example, polystyrene and ethyl cellulose, are dissolved in the same solvent, for example, benzene. In such cases phase separation sets in at very low solute concentrations and the two phases formed contain disproportionate amounts of the two solutes. A comprehensive study of such systems has been made in particular by Dobry and Boyer-Kawenoki[1]. Taking as example the system polystyrene – ethyl cellulose – benzene used in our experiments, it is found that a solution containing only 2–3 per cent total polymer (degree of polymerization about 1,000) is separated into two phases at room temperature. These phases again each contain 97–98 per cent benzene, but one is largely a solution of polystyrene with only a little ethyl cellulose, and the other is an ethyl-cellulose solution with relatively little polystyrene.

The two phases obtained in this manner are similar in their behaviour to the phases obtained when two partially miscible liquids, for example, water and amyl alcohol, are mixed together.

The systems are dependent on temperature and, in the particular case of the system polystyrene – ethyl cellulose – benzene considered here, the mutual solubility of the phases is increased as the temperature is raised. More ethyl cellulose is dissolved by the phase rich in polystyrene and more polystyrene by

the phase rich in ethyl cellulose. The compositions of the two phases of the unstirred system therefore approach each other as the temperature is increased, and for each given overall composition there exists a well-defined 'critical' solution temperature T_c at which phase separation just ceases and above which the system is homogeneous.

Overall concentration (% w/w)			T_c (°C.)	Relative volume of phases at 21·7° C. i.e., T_c–10° C.(vol. %)	
Benzene	Polystyrene	Ethyl cellulose		I	II
97·1	1·14	1·80	31·7	47	53

At 22° C. the above system is obviously 10° C. below its critical temperature and is separated into two phases. If, however, a velocity gradient of $q = 200$ sec.$^{-1}$ is maintained in this system (at 22° C.) a homogeneous one-phase solution results. There exists, in fact, a quantitative relationship between the number of degrees, ΔT (°C.), by which the system is below its critical solution temperature, and the rate of shear q (sec.$^{-1}$) which can completely reverse the phase separation at the temperature $T_c - \Delta T$. In the case of the particular system investigated by us, this is :

$$q = 20\ \Delta T. \qquad (1)$$

In order to illustrate the rates of shear necessary according to (1) to produce a noticeable shift in the critical solution temperature, consider a Couette apparatus, that is, a cylindrical drum (say, 5 cm. in diameter), rotating in a concentric cup (say 7 cm. in internal diameter), the interspace being filled with solution, and assume that the angular speed of rotation of the drum is 1 revolution per second. (These particular dimensions apply to the apparatus used by us. It is worth noting, by the way, that, as the viscosity of the solution is 0·11 poise, laminar flow conditions prevail up to about $q = 270$ sec.$^{-1}$.) Such a speed, which could easily be maintained by hand, would in this case correspond to a rate of shear $q = 27$ sec.$^{-1}$ and would, according to (1), suffice to change the critical solution temperature by 1·3° C.

The changes observed in this manner are completely reversible, that is, the system separates again (becomes turbid) as soon as the rate of shear drops below the values given by (1). The effect of the field of flow is thus to make the homogeneous system stable at temperatures at which the homogeneous system of the same composition, but at rest, is metastable. This means that the free energy of the stirred homogeneous system, and with it also the free energy of certain of its components, must be larger than the corresponding quantities of the resting, separated system at the same temperature.

The reversal of phase separation in a field of flow is intimately connected with the large interfacial area which is created when the separated system is gently stirred. An immediate break-up into fine drops takes place, their final size being determined by the hydrodynamics of flow. By simple dimensional analysis the mean linear dimension r of the largest drop which can exist in a laminar field of flow of velocity gradient q can be related to the interfacial tension σ and the viscosity η of the surrounding medium. We find :

$$r = \text{const.} \frac{\sigma}{\eta q}, \qquad (2)$$

where the constant of proportionality is dimensionless and of the order of 0·15 in cases where the difference between the viscosity of the drop and the viscosity η of the surrounding medium is small[2].

If it is assumed that the interfacial tension is left unaffected by the decrease in drop radius, equation (2) represents the effect of the field of flow on drop size for all values of q. Our experiments have shown that this is true only initially, that is, at low rates of shear, and only up to drop sizes of about 10^{-3} cm. Further decrease in drop size is found to result in a rapid decrease of interfacial tension and a complete reversal of the phase separation.

Experimentally, we infer the disappearance of the second phase from the disappearance of turbidity, that is, of optical inhomogeneity in the system. If this optical homogeneity had been produced according to (2), that is, by a mere reduction in size of drop, the necessary rate of shear would, obviously, have had to be 1,000 times greater than that required for $r = 10^{-2}$ cm. Experimentally, however, we find a factor of only about 10, clearly showing, as stated, that a breakdown of σ must have occurred at some intermediate size of drop.

Theoretically, we can explain this phenomenon as follows. The interface between two phases is not infinitely thin, but represents a transition zone of inhomogeneous composition, of finite thickness and volume. If this thickness is ε cm. and if there are f sq. cm. of interfacial area per 1 c.c. of the system, then the interface occupies a fraction $f\varepsilon$ of the total volume. The interfacial tension may be defined as the free energy necessary to form ε c.c. of 'interface' out of the non-interfacial region of the system. The existence of f sq. cm. of interface therefore implies a free energy increase of $f\sigma$ ergs/c.c. relative to the state of the system in which $f = 0$. An isothermal approach in composition of the two phases would reduce σ, and therefore $f\sigma$, but would at the

same time increase the free energy in the $(1 - f\varepsilon)$ c.c. not occupied by the interface. So long as f is small ($f\varepsilon \ll 1$), the change in composition, which must accompany a reduction in $f\sigma$, will therefore severely restrict this effect. In our case, ε is determined by the dimensions of the coiled polymer in solution and is, thus, of the order 10^{-5} cm. When the size of drop r is therefore smaller than about 10^{-3} cm., the interfacial volume, $f\varepsilon$, becomes comparable with 1, and an approach in composition leading to a reduction in total free energy, as well as in $f\sigma$, becomes possible. At constant rate of shear, q, this decrease in σ brings with it, as secondary effect, a further reduction in size of drop (see (2)), and, due to the increased value of f, a renewed change in composition. Equilibrium is reached between these tendencies at lower rates of shear, but there exists a critical value of q at which these effects so reinforce each other that there is a complete resolution of all differences in composition and a complete reversal of the phase separation.

In the above, we have given a somewhat simplified description. Thus, at constant q and σ, there can be a reduction in f, and therefore of $f\sigma$, by a solution of some of the dispersed phase in the surrounding medium (analogous to the increase of vapour pressure of small droplets by capillarity). This reduction in f is, however, in our case, where dispersed phase and surrounding medium are of roughly equal volume, accompanied by a correspondingly large change in composition. The two effects, the one mentioned now and that discussed in the preceding paragraph, are therefore on closer inspection seen to be non-separable phenomena.

It is clear that, as the size of drop, r, becomes comparable with ε, the definition of r, and with it the concept of capillarity, rapidly lose precision. The homogenization process at this stage may be pictured as a gradual replacement of the non-interfacial $(1-f\varepsilon)$-regions by the interfacial $(f\varepsilon)$-regions of the system (the interface will, in general, 'consume' one phase faster than the other). As $f\varepsilon \to 1$, the concentration gradient in the interface, for energetic reasons, tends to decrease, leading eventually to the homogeneous solution as the most stable state. The use of f and σ has here only a symbolic significance.

We have emphasized the fact that the homogeneous system has a larger free energy than the separated, unstirred system at the same temperature (as revealed by spontaneous demixing as soon as stirring is stopped). The otherwise unstable homogeneous state is thus maintained at the expense of a continuous degradation of mechanical into thermal

energy in the field of flow. The rate at which thermal energy is produced under the conditions described by equation (1) in a medium of viscosity $\eta = 0{\cdot}11$ poise is obviously $\eta q^2 = 44(\Delta T)^2$ erg/c.c. sec. On the other hand, the time during which a noticeable demixtion would take place in the solution is roughly equivalent to the time, t, taken by the coiled polymer to diffuse a distance of the order of its end-to-end distance ($\sim 5 \times 10^{-6}$ cm.). Remembering that the diffusion constant of the polymer in a medium of this viscosity is about 10^{-8} cm.^{2}/sec., $t = \frac{1}{2}(5 \times 10^{-6})^2/10^{-8} = 1{\cdot}25 \times 10^{-3}$ sec. and the thermal energy produced in this time equals $5 \times 10^{-2}(\Delta T)^2$ erg/c.c. This we compare with the free energy required to homogenize 1 c.c. of the demixed system when it is ΔT° below T_c. Using the theory of Scott[1], it is easily shown that this energy is of the same magnitude, being in the present case about $6{\cdot}2 \times 10^{-2}(\Delta T)^2$ erg/c.c. The rate at which thermal energy is produced from mechanical energy in the field of flow is thus, indeed, sufficient to prevent the homogeneous system from demixing.

From the above it becomes clear that the effects observed (shift in solubility and critical solution temperature) need not be specific to systems with macromolecular components, although it can be seen why they are particularly large in such cases. Fundamentally the same situation arises in all liquid–liquid equilibria as well as in the case of liquid–vapour transitions and the corresponding critical phenomena. [Dec. 6.

[1] Dobry, A., and Boyer-Kawenoki, F., *J. Polymer Sci.*, **2**, 90 (1947). See also Scott, R. L., *J. Chem. Phys.*, **17**, 279 (1949).

[2] For further details, see Silberberg, A., and Kuhn, W., *J. Polymer Sci.* (in the press).

CURRICULUM VITAE

I, Alexander Silberberg, of Johannesburg, South Africa, was born on the 24th February, 1923, in Vienna, Austria, the son of Joseph Silberberg, mechanical engineer, also of Johannesburg, and his wife, the late Josephine Konstantinowsky. After finishing primary school in Vienna I emigrated with my family to South Africa, where I continued my schooling at the Marist Brothers' College, Johannesburg, and in 1940 passed the matriculation examination of the South African Universities' Joint Matriculation Board with First Class Distinction. In February 1941 I registered in the Faculty of Engineering, Branch of Chemical Engineering, of the University of the Witwatersrand, Johannesburg, and attended and passed all the courses prescribed by regulation. For the years 1941, 1942, and 1944 I was elected a Scholar of the University and on the 17th March, 1945, I graduated with the degree of Bachelor of Science in Engineering. Thereafter I served till 1946 in the Radar Section of the South African Armed Forces and then spent two years working as chemical engineer before coming to Switzerland during the summer of 1948. In October 1948 I registered in the University of Basle and commenced research under the direction of Prof. W. Kuhn on the thesis submitted. While at Basle I attended the lectures of Prof. W. Kuhn, Prof. A. Ostrowsky, Prof. A. Speiser, Prof. M. Fierz, Prof. H. Kuhn, Prof. H. Mohler and Dr. P-D. F. Grün.